$C(...)$	correction term in eq 1
D_{AB}	mutual diffusion coefficient (m^2/s)
D_{AB}^{SHS}	mutual diffusion coefficient for smooth hard spheres
D_{AB}^{HSG}	mutual diffusion coefficient for a low-density hard sphere gas
D°_{AB}	mutual diffusion coefficient at infinite dilution
De	Dean number
F	correction term in eq 1
$g(\sigma_{AB})$	radial distribution function
L	length of the dispersion column
k	Boltzmann constant
k_1, k_2	calibration constants in eq 15
K	Taylor diffusion coefficient
m	mass of solute in the sample injected
m_A, m_B	molecular masses of solute and solvent
M	molecular weight
n	number density (molecules/volume)
n_A, n_B	number densities of solute and solvent
N	Avogadro number
P	pressure
R	radius of the tube
R_c	helix radius
Re	Reynolds number
Sc	Schmidt number
t	time
t_R	residence time
T	absolute temperature (K)
u	velocity at x frame of reference
V	molar volume
V_D	molar volume at which the diffusion is frozen
V_0	closed-packed hard-sphere volume
$W_{1/2}$	the width at half the peak height
x	axial coordinate

Greek Letters

γ	constant in eq 8
μ	viscosity of solution
ρ	density

σ_A, σ_B	molecular diameters of solute and solvent
σ_{AB}	average collision diameter of the solute and solvent molecules
ψ	packing factor for hard-sphere assemblies
Ω	period of oscillation

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Excess Properties for 1-Butanethiol + n-Heptane, Cyclohexane, Benzene, and Toluene. 1. Excess Molar Volumes at 283.15 and 298.15 K

Gregory C. Allred,* J. William Beets,† and William R. Parrish

Phillips Petroleum Company, Bartlesville, Oklahoma 74004

This paper reports densities and excess molar volumes at 283.15 and 298.15 K, at atmospheric pressure, for binary mixtures of 1-butanethiol + n-heptane, cyclohexane, benzene, and toluene. The excess molar volumes are less than 0.607 cm^3 mol^{-1}, or 0.56% of the mixture molar volume. The excess molar volumes increase with increasing temperature for 1-butanethiol + n-heptane; they decrease with increasing temperature for the other three systems. Excess molar volumes for 1-butanethiol + aromatic systems are smaller than for paraffinic systems, with the maximum values for toluene being 0.007 cm^3 mol^{-1}.

* Author to whom correspondence should be addressed.
† Present address: School of Medicine, University of Oklahoma, Norman, OK.

Introduction

Sulfur compounds, and their behavior with hydrocarbons, are important in the petroleum and chemical industries. An understanding of mixture nonidealities is needed to design processes to remove sulfur compounds from petroleum, to purify sulfur compounds for use as chemical intermediates, and to solve environmental problems. Excess molar volumes, together with excess enthalpies and activity coefficients, when used to develop and evaluate molecular models, help us to understand the effects of molecular size and molecular interactions as the basis of nonideal mixing behavior. This understanding, together with experimental data, is required for the development of practical models and correlations for design calculations.

We know of no published density data for binary mixtures of thiols (mercaptans) with hydrocarbons. Here we present den-

Table I. Sources, Purities, and Densities, ρ, of Chemicals

chemical	source	stated purity/mol %	ρ/(g cm^{-3}) measured 283.15 K	298.15 K	ref 4 298.15 K
1-butanethiol	Phillips	98	0.850 82	0.836 50	0.836 74
n-heptane	Phillips	99	0.692 10	0.679 48	0.679 46
cyclohexane	Aldrich	99.9	0.787 76	0.773 77	0.773 89
benzene	Aldrich	99+	0.889 40	0.873 46	0.873 6
toluene	Aldrich	99.9	0.875 79	0.861 94	0.862 2

sities and excess molar volumes for binary mixtures of 1-butanethiol + n-heptane, cyclohexane, benzene, and toluene.

Experimental Section

Densities were determined at 283.15 and 298.15 K, at atmospheric pressure, with use of an Anton-Paar DMA 602 HT vibrating-tube densimeter. This technique requires two density standards; we used freshly boiled, deionized, distilled water and dry nitrogen. The density of water was calculated from the correlation given by Kell (1) and that of nitrogen from the modified Berthelot equation given by Ott et al. (2). The temperature was measured with a thermistor thermometer inserted into a thermowell in the glass densimeter cell. The densimeter temperature was known to within ±0.1 K and was held constant within ±0.01 K.

Table I gives sources, purities as received from the supplier, measured densities, and published densities for all the chemicals used in this investigation. We distilled the 1-butanethiol and n-heptane under nitrogen in a column packed with glass helices and discarded the first 20% and the last 10% of each distillation batch. Cyclohexane, benzene, and toluene were used as received. We degassed all chemicals just prior to use by placing the unopened containers in an ultrasonic bath.

Mixtures were prepared by mass in evacuated, 22-mL glass vials with Teflon-lined rubber septum caps. The vials were weighed again before each mixture sample was withdrawn, and the mole fraction of each component in the liquid phase was calculated and corrected for evaporation into the vapor space by using the measured liquid density, the ideal gas law, and activity coefficient data, which will be published later. The total correction was always less than 0.000 06 mole fraction. The reported values are the average mole fraction and density for two or three replicate density determinations on each mixture.

The excess molar volume

$$V^E = V - (x_1 V_1 + x_2 V_2) \tag{1}$$

was obtained from the density ρ of each mixture according to the relation

$$V^E = (x_1 M_1 + x_2 M_2)/\rho - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2) \tag{2}$$

where V is the molar volume of the mixture and x_i is the mole fraction, M_i is the molecular weight, and ρ_i is the density of pure component i.

We used a Monte Carlo error analysis method to estimate reproducibility in mixture mole fraction, density, and excess molar volume based on the standard deviations of the principal independent variables. The relative standard deviations of the independent variables were estimated as 0.0002, 0.000 01, 0.05, 0.000 01, and 0.000 004 for mixture component mass, density of water, density of nitrogen, densimeter vibrational period for nitrogen, and densimeter vibrational period for liquid, respectively. The resulting estimated standard deviations of the calculated quantities were 0.000 03, 0.000 02 g cm^{-3}, and 0.0038 cm^3 mol^{-1} for mole fractions, mixture densities, and

Table II. Densities, ρ, and Excess Molar Volumes, V^E, for 1-Butanethiol (1) + Hydrocarbon (HC, 2)

x_1	ρ/ (g cm^{-3})	V^E/ (cm^3 mol^{-1})	x_1	ρ/ (g cm^{-3})	V^E/ (cm^3 mol^{-1})
			$T = 283.15$ K		
HC = n-Heptane			HC = Cyclohexane		
0.137 23	0.707 64	0.199	0.101 47	0.792 07	0.276
0.231 23	0.719 14	0.302	0.187 13	0.796 16	0.446
0.337 85	0.733 33	0.347	0.282 81	0.800 83	0.620
0.423 14	0.745 44	0.364	0.385 17	0.807 08	0.640
0.536 20	0.762 65	0.359	0.479 72	0.813 29	0.602
0.618 41	0.776 12	0.329	0.595 64	0.820 92	0.555
0.726 20	0.795 04	0.268	0.688 93	0.827 38	0.477
0.826 68	0.814 12	0.189	0.790 08	0.834 67	0.360
0.901 03	0.829 21	0.119	0.893 56	0.842 45	0.202
HC = Benzene			HC = Toluene		
0.096 18	0.883 96	0.105	0.115 27	0.872 92	−0.003
0.190 20	0.879 20	0.174	0.214 33	0.870 43	−0.002
0.274 65	0.875 28	0.214	0.311 92	0.867 97	−0.001
0.368 38	0.871 35	0.228	0.411 92	0.865 43	0.003
0.465 60	0.867 54	0.231	0.503 47	0.863 14	0.004
0.569 08	0.863 85	0.209	0.606 94	0.860 55	0.005
0.666 12	0.860 60	0.179	0.709 09	0.857 99	0.007
0.775 17	0.857 18	0.132	0.797 73	0.855 78	0.007
0.885 40	0.853 94	0.074	0.899 42	0.853 30	0.001
			$T = 298.15$ K		
HC = n-Heptane			HC = Cyclohexane		
0.137 23	0.694 74	0.224	0.101 47	0.778 13	0.273
0.231 23	0.706 08	0.334	0.187 14	0.782 28	0.436
0.337 85	0.720 11	0.378	0.282 82	0.787 49	0.538
0.423 14	0.732 08	0.394	0.385 19	0.793 44	0.596
0.536 21	0.749 15	0.380	0.479 74	0.799 24	0.607
0.618 41	0.762 49	0.345	0.595 65	0.806 89	0.551
0.726 20	0.781 28	0.273	0.688 93	0.813 33	0.470
0.826 68	0.800 20	0.186	0.790 09	0.820 60	0.347
0.901 03	0.815 18	0.111	0.893 57	0.828 28	0.193
HC = Benzene			HC = Toluene		
0.096 18	0.868 37	0.094	0.115 27	0.859 00	−0.002
0.190 20	0.863 87	0.155	0.214 32	0.856 47	−0.003
0.274 67	0.860 18	0.187	0.311 91	0.853 95	0.000
0.368 39	0.856 36	0.207	0.411 92	0.851 39	0.001
0.465 62	0.852 77	0.201	0.503 47	0.849 05	0.003
0.569 09	0.849 20	0.184	0.606 94	0.846 43	0.002
0.666 13	0.846 06	0.155	0.709 08	0.843 82	0.005
0.775 18	0.842 74	0.113	0.797 72	0.841 55	0.007
0.885 40	0.839 60	0.060	0.899 41	0.839 04	−0.001

excess molar volumes, respectively. The estimated standard deviation in V^E exceeds the calculated values for V^E for most 1-butanethiol + toluene mixtures.

Results and Discussion

Densities and excess molar volumes for the 1-butanethiol + (n-heptane, cyclohexane, benzene, or toluene) system are given in Table II. We correlated excess molar volume as a function of composition with equations of the form

$$V^E/(\text{cm}^3 \text{ mol}^{-1}) = x(1-x)\sum A_i(1-2x)^{i-1} \quad i = 1, 2, 3, \ldots \tag{3}$$

where x is the mole fraction of 1-butanethiol. Coefficients A_i

Table III. Coefficients of Equation 3

mixture	A_1	A_2	A_3	n^a	s^b
		T = 283.15 K			
1-butanethiol +					
n-heptane	1.4538 (0.0114)^c	0.2865 (0.0227)	0.1381 (0.0526)	9	0.0050
cyclohexane	2.4712 (0.0546)	0.7548 (0.1062)	0.2913 (0.2475)	9	0.0234
benzene	0.8988 (0.0040)	0.3132 (0.0080)	0.1072 (0.0186)	9	0.0017
toluene	0.0177 (0.0030)	−0.0406 (0.0059)	−0.0293 (0.0138)	9	0.0013
		T = 298.15 K			
1-butanethiol +					
n-heptane	1.5553 (0.0111)	0.4496 (0.0221)	0.0980 (0.0513)	9	0.0049
cyclohexane	2.3888 (0.0102)	0.5943 (0.0198)	0.1852 (0.0461)	9	0.0044
benzene	0.7921 (0.0034)	0.3045 (0.0067)	0.0661 (0.0156)	9	0.0015
toluene	0.0111 (0.0048)	−0.0300 (0.0095)	−0.0169 (0.0223)	9	0.0021

^{a} Number of data points, each of which is an average of two or three measurements. ^{b} Standard deviation of fit, cm^3 mol^{-1}. ^{c} Standard deviation of coefficient determined from regression.
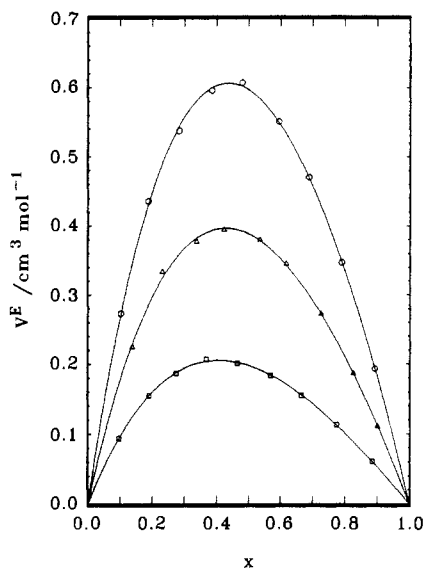

Figure 1. Excess molar volume V^E of 1-butanethiol + hydrocarbon at 298.15 K as a function of the mole fraction x of 1-butanethiol: -O-, cyclohexane; -△-, *n*-heptane; -□-, benzene.

Figure 2. Excess molar volume V^E of 1-butanethiol or 1-butanol + hydrocarbon at 298.15 K as a function of the mole fraction x of 1-butanethiol or 1-butanol: -△-, 1-butanethiol + *n*-heptane; --O--, 1-butanethiol + toluene; —, 1-butanol + *n*-heptane (ref 5); --, 1-butanol + toluene (ref 6).

for each system were determined by using a maximum-likelihood linear regression procedure (*3*). Coefficients and standard deviations from the regression are given in Table III.

Excess molar volumes at 298.15 K and smooth curves calculated from eq 3 are shown in Figures 1 and 2. Excess molar volumes for 1-butanethiol + (*n*-heptane, cyclohexane, and benzene) are positive, and for 1-butanethiol + toluene the excess molar volume is positive at the thiol-rich end of the composition scale and negative for mixtures with a mole fraction of thiol less than about 0.3. For all of these mixtures except 1-butanethiol + *n*-heptane, the excess molar volume decreases with increasing temperature.

Thiols are analogous to alcohols; therefore we might expect them to show similar trends in their mixture behavior. Excess volumes for the 1-butanol + hydrocarbon systems are shown in Figure 2. When V^E for 1-butanethiol + hydrocarbon mixtures are compared with V^E for 1-butanol + hydrocarbon mixtures, the change in V^E follows the same trend for both 1-butanethiol and 1-butanol when going from the paraffinic *n*-heptane toward the more aromatic toluene. But while V^E is positive at the toluene-rich end of the scale for 1-butanol, it is negative for the analogous 1-butanethiol mixture.

Conclusions

Excess molar volumes at 283.15 and 298.15 K for binary mixtures of 1-butanethiol + (*n*-heptane, cyclohexane, benzene, or toluene) are small, and mostly positive; all are less than
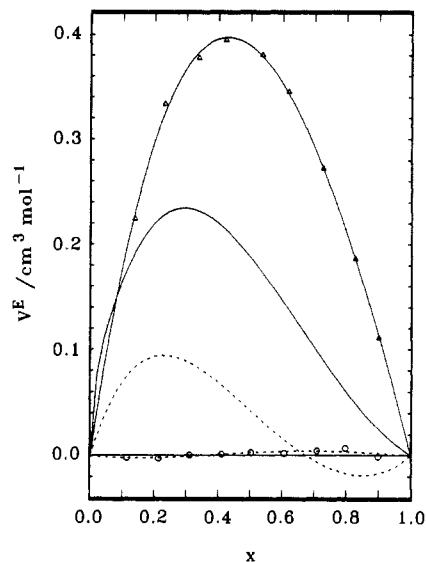
0.607 cm^3 mol^{-1}, or 0.56% of the mixture molar volume. The estimated standard deviation of V^E for the 1-butanethiol/hydrocarbon mixtures is 0.004 cm^3 mol^{-1}. Excess molar volumes for 1-butanethiol + aromatic systems are smaller than for paraffinic systems, which is indicative of stronger intermolecular association for thiol + aromatic systems.

Trends in the excess molar volumes for 1-butanethiol + (*n*-heptane or toluene) are qualitatively similar to those of the analogous 1-butanol + hydrocarbon systems. The differences are (1) excess molar volumes for 1-butanethiol + toluene are much smaller than those for 1-butanol + toluene, while excess molar volumes for 1-butanethiol + *n*-heptane are larger (above 0.1 mole fraction) than those for 1-butanol + *n*-heptane and (2) excess molar volumes have the opposite sign for the 1-butanethiol/toluene system, i.e., at the toluene-rich end of the composition scale, the excess molar volumes are negative in the 1-butanethiol system, but positive in the 1-butanol system.

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Isothermal Vapor–Liquid Equilibria for *n*-Hexane–Methyl Methacrylate, Methyl *n*-Propyl Ketone–Acetic Acid, *n*-Pentane–Methyl Acetate, and Ethyl Acetate–Acetic Anhydride

Benjamin C.-Y. Lu, * **Takeshi Ishikawa, and George C. Benson**

Department of Chemical Engineering, University of Ottawa, Ottawa, Canada K1N 9B4

Isothermal vapor–liquid equilibria were measured for mixtures of *n*-hexane with methyl methacrylate and methyl *n*-propyl ketone with acetic acid at 333.15 K, *n*-pentane with methyl acetate at 298.15 K, and ethyl acetate with acetic anhydride at 348.15 K. The experimental results for each system were correlated by using the method of Barker to fit the total pressure and liquid composition values. A binary azeotrope was found for *n*-pentane–methyl acetate.

Introduction

A previous paper (*1*) from our laboratory presented vapor–liquid equilibria for mixtures of cyclohexane with methyl methacrylate. Such data are of interest in ester interchange reactions between methyl methacrylate and alcohols.

The present paper reports similar isothermal studies of four diverse systems: (A) *n*-hexane (1)–methyl methacrylate (2) at 333.15 K, (B) methyl *n*-propyl ketone (1)–acetic acid (2) at 333.15 K, (C) *n*-pentane (1)–methyl acetate (2) at 298.15 K, and (D) ethyl acetate (1)–acetic anhydride (2) at 348.15 K, which are also of relevance in esterification and related processes. Equilibria for system C have been reported previously (*2*, *3*); we are not aware of other comparable investigations.

Experimental Section

Isothermal vapor–liquid equilibria for the four binary systems were established in a modified Dvorák and Boublík recirculating still (*4*) operated as described previously (*4*, *5*). The auxiliary equipment for measuring temperature and pressure was the same as used by Hull and Lu (*1*). Analyses of the condensed vapor and liquid samples were based either on determinations of density made with an Anton-Paar K.G. (Model DMA 02A) digital densimeter or on measurements of refractive index made with a Bausch & Lombe Model Abbe-3L precision refractometer. In either case, a calibration curve was established from measurements on a series of mixtures of known composition.

The component liquids are described in Table I, where their physical properties (density and/or refractive index and vapor pressure) are given, along with values from the literature (*6–9*) for comparison. In all cases, these materials were used for the vapor–liquid studies without further purification.

Results and Discussion

The experimentally determined pressures, *P*, and liquid and vapor compositions, x_1 and y_1, for the isothermal equilibrium

of the mixtures at temperature, *T*, are listed in Tables II–V and plotted in Figures 1–4. In each case, the method of obtaining the compositions (either from density or refractive index) is indicated in the footnote of the table, along with estimates of the uncertainties ($\epsilon(T)$, $\epsilon(P)$, $\epsilon(x_1)$, and $\epsilon(y_1)$) in the primary measurements.

The results for each system were correlated by the Barker method (*10*), assuming a Redlich–Kister form

$$G^E = x_1 x_2 \sum_{j=1}^{n} c_j (x_2 - x_1)^{j-1} \tag{1}$$

for the excess molar Gibbs energy, G^E, of the mixture. The corresponding activity coefficients, γ_i, in the liquid phase are

$$\gamma_i = \exp\{[G^E + (1 - x_i)(dG^E/dx_i)]/RT\} \tag{2}$$

and the pressure and vapor compositions are given by

$$P = \gamma_1 p_1' + \gamma_2 p_2' \tag{3}$$

and

$$y_i = \gamma_i p_i'/P \tag{4}$$

where

$$p_i' = x_i P_i^{\circ} \exp\{[(V_i^{\circ} - B_{ii})(P - P_i^{\circ}) + (B_{11} + B_{22} - 2B_{12})(1 - y_i)^2 P]/RT\} \tag{5}$$

Values of the coefficients, c_j, were determined by an iterative least-squares analysis in which eq 3 was fitted to the observed (x_1, P) data. At each step in the calculation, y_i was computed from eq 4. The quantities P_i°, B_{ii}, and V_i°, in eq 5, are the vapor pressure, second virial coefficient, and liquid molar volume of pure component *i* at temperature *T*, and B_{12} is the cross second virial coefficient in the mixture. The experimental P_i° listed in Table I were used in the calculation. The footnotes of Tables II–V summarize the values of V_i° and B_{ii}. In most cases, these were taken from the literature (*6*, *9*, *11–15*); however, experimental values of B_{ii} for methyl methacrylate and acetic anhydride were not available. Values of B_{ii} for those components and of B_{12} for all of the mixtures were estimated by the method of Hayden and O'Connell (*16*).

The coefficients c_j, obtained from the least-squares analysis of the (x_1, P) data for each system, are listed in Table VI. Values of $G^E(x_1)$, calculated from eq 1, are given in Tables II–V, along with the deviations of the calculated *P* and y_1 values from the corresponding experimental results. The standard deviations σ_p and σ_y for system A are smaller than the estimated uncertainties of the measurements. However, σ_p and